

Alteration of paramagnetic centers in MoO₃ and TiO₂ : MoO₃ composites after heating under reducing atmosphere

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Individual MoO₃ as well as TiO₂ : MoO₃ composites find wide application as catalysts in dehydration processes and as sensing materials for detection of under explosive concentrations of hydrogen. Investigation of paramagnetic centers that can act as H₂ adsorption sites in MoO₃ and TiO₂ : MoO₃ composites is an urgent scientific task.

In the work MoO₃ was synthesized by precipitation with HNO₃ from (NH₄)₆Mo₇O₂₄ saturated solution. TiO₂ : MoO₃ nanocomposites with MoO₃ content under 5 mol.% were synthesized by sol-gel method. The oxide materials were heated at 450 °C. Paramagnetic centers in the materials were investigated by ESR spectroscopy (room temperature, air, radiation power 200 mW).

It was established, that ESR spectrum of individual MoO₃ (Fig. a) contains eight resonance lines corresponding to six paramagnetic centers: (Mo-O)⁵⁺ (resonance line 1) and O⁻ hole centers (line 2), adsorbed O₂⁻ radicals (line 3), F-centers (line 4), 6-fold coordinated Mo⁵⁺ in axially distorted oxygen environment (lines 5, 6, 8), [(Mo=O)³⁺-(O²⁻)₃] molybdenyl centers (line 7). In case of TiO₂ : MoO₃ composite in the ESR spectrum (Fig. c) only three resonance lines can be registered, which correspond to two types of paramagnetic centers – 6-fold coordinated Mo⁵⁺ in axially distorted oxygen environment (lines 9, 11), and [(Mo=O)³⁺-(O²⁻)₃] molybdenyl centers (line 10). Reduction of the quantity of resonance lines in ESR spectra of multioxide material can be explained by the presence of intense dipole-dipole interaction between Ti³⁺ paramagnetic centers that leads to the hard broadening of these resonance lines in the spectrum up to complete disappearance of all possible resonance lines in the spectrum of individual TiO₂.

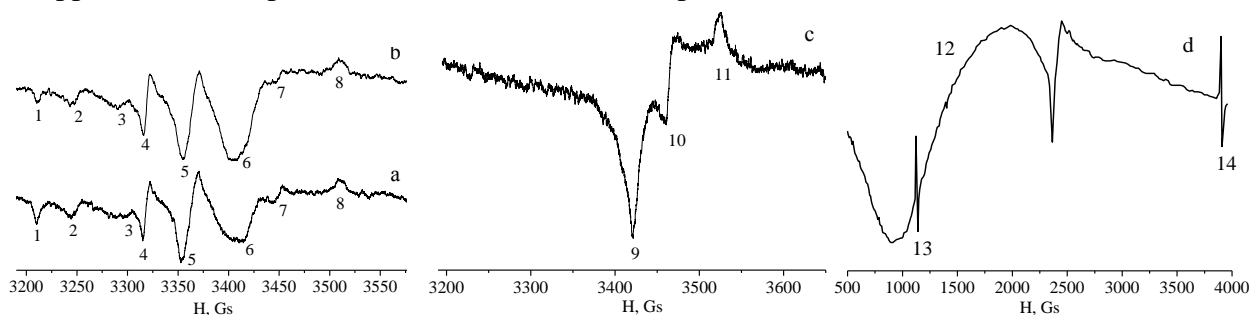


Fig. ESR spectra of MoO₃ before hydrogen treatment (a), immediately after H₂ treatment (b); TiO₂ : MoO₃ composite before H₂ treatment (c) and after prolonged H₂ treatment (d)

Heating under reducing atmosphere was lead at 300 °C in hydrogen. The following ESR investigation of the materials (Fig. b) revealed a decrease in the intensity and the amplitude of (Mo-O)⁵⁺ centers and [(Mo=O)³⁺-(O²⁻)₃] molybdenyl centers both in individual MoO₃ and TiO₂ : MoO₃ composites. Such alteration can be due to the processes of hydrogen adsorption on these paramagnetic centers. Moreover intensity of Mo⁵⁺ paramagnetic centers line sharply increases after heating in H₂ with subsequent gradual lowering to the initial values in air both in MoO₃ and TiO₂ : MoO₃ composite. This fact indicates that Mo⁶⁺ to Mo⁵⁺ reduction in the hydrogen atmosphere takes place with the following reverse oxidation by the atmospheric oxygen. When heating time is increased, the quantity of Mo⁵⁺ centers in TiO₂ : MoO₃ composite enhances so, that in the ESR spectra ferromagnetic component can be observed (Fig. d, broad line 12) (lines 13, 14 – calibrating Al₂O₃ : Cr crystal). Under these conditions TiO₂ : MoO₃ composite can be treated as substitutional solution of Mo⁵⁺ ions in diamagnetic TiO₂ matrix, where paramagnetic Mo⁵⁺ centers form a sort of regularized structure.